

Degradation Model of Optical Characteristics of ZnO-Pigmented White Paint by Electron Radiation

Tian Hai, Yang Shengsheng, Jr., and Wang Yi

Abstract—Based on an analysis of the mechanism of degradation of optical characteristics of the ZnO-pigmented white paint by electron irradiation, a model of single molecular color centers is built. An equation that explains the relationship between the changes of variation of the ZnO-pigmented white paint's spectrum absorptance and electron fluence is derived. The uncertain parameters in the equation can be calculated using the curve fitting by experimental data. The result indicates that the model can be applied to predict the degradation of optical characteristics of ZnO-pigmented white paint by electron radiation.

Keywords—ZnO-pigmented white paint; effects of electron radiation; optical characteristics degradation; prediction model.

I. INTRODUCTION

Thermal control of spacecraft is necessary to restrict the temperature excursions within limits imposed by the payload. Passive thermal control uses the thermal radiative properties of the exterior surface of the space vehicle to obtain an optimum operating temperature by achieving a balance between heat input and output^[1]. Since the primary external heat input is from solar radiation, the ratio of the solar absorptance (α_s) to thermal emittance (ϵ) of the exterior surfaces governs the equilibrium temperature of the spacecraft. Thermal control coatings are subject to degradation caused by vacuum and ultraviolet, electrons, solar protons, micrometeoroids, and contamination^[2].

ZnO-pigmented white paints are commonly utilized on spacecraft because of their optical properties and stability to the space environment. However, ZnO-pigmented white paints are degraded by exposure to high vacuum and long-term particle radiation. This degradation results in an increase of the solar absorptance of the coating and thus reduces its effectiveness as a passive-thermal-control surface. Therefore, there is a need to evaluate the degradation of the white coating's performance on satellites for the duration of their active life.

Based on an analysis of the mechanism of degradation of optical characteristics of the ZnO-pigmented white paint by electron irradiation, a single molecular color centers model is

built and an equation that explains the relationship between the changes of variation of the material's spectrum absorption ($\Delta\alpha_s$) and electron fluence is derived. The uncertain parameters in the equation can be calculated using the curve fitting by the experimental data. The result indicates that the model can be applied to predict the degradation of ZnO-pigmented white paint's optical characteristics by electron radiation.

II. THE MECHANISM OF DEGRADATION OF OPTICAL CHARACTERISTICS OF THE ZnO-PIGMENTED WHITE PAINT BY ELECTRON IRRADIATION

For the lower energy (smaller than 100 keV) electron radiation, the damages mainly come from elastic collision and inelastic collision^[3]. In the inelastic collision, incident electrons transfer energy to the conduction band electrons. The conduction band electrons absorb energy and jump to conduction band, and then electron-hole pairs are created. This is ionization damage effect^[3,4]. In the elastic collision, incident electrons transfer energy to the color center in the forbidden band, then Frenkel pairs are created and color center level changes.

Under electron irradiation, some transition electrons are captured by the color center level in the forbidden band, then part of the intrinsic color center $V_o^{\bullet\bullet}$ transformed into $V_{o,i}^{\bullet}$ in the forbidden band and the number of the V_o^{\bullet} increases. Two new kinds of color center (R_1 and R_2) are created by electron irradiation. R_1 is the symmetrical paramagnetic center and R_2 is the Centro symmetric symmetrical paramagnetic center. V_o^{\bullet} and R_2 are effective color centers of ZnO. The density of the V_o^{\bullet} and R_2 increases by electron irradiation. Therefore, conduction band electrons absorb visible light photons and jump to V_o^{\bullet} or R_2 energy level, or the probability that bound electrons of V_o^{\bullet} and R_2 color center jump to conduction band by absorbing visible light photons increases^[5].

The photon energy of near infrared region is not big enough to induce that conduction band electrons jump to V_o^{\bullet} or R_2 energy level, or the bound electrons in the V_o^{\bullet} and R_2 color center level jump to conduction band. However, the bound electrons near the bottom of R_1 energy level can jump from low energy to high energy level. It also can result in that optical characteristics of the ZnO degenerate.

F. A. Tian Hai is with the Science and Technology on Vacuum & Cryogenics Technology and Physics Laboratory, No.97, Wei Yuan Road, Chengguan District, Lanzhou City, GanSu Province, China (phone: 86-931-4585044; fax: 86-931-8265391; e-mail: tianhaicn@gmail.com).

S. B. Yang Shengsheng, Jr., is with the Science and Technology on Vacuum & Cryogenics Technology and Physics Laboratory, No.97, Wei Yuan Road, Chengguan District, Lanzhou City, GanSu Province, China).

T. C. Wang Yi is with the Science and Technology on Material Performance Evaluating in Space Environment Laboratory, No.97, Wei Yuan Road, Chengguan District, Lanzhou City, GanSu Province, China).

In conclusion, the density of color centers in the forbidden band increases by electron radiation and many areas that absorb visible light and near infrared light photons are produced. Therefore, the solar absorptance (α_s) of the ZnO-pigmented white paint increases and the color of the paint darkles. The density of color center V_o^\bullet in the forbidden band increases is the primary reason that the optical characteristics of the ZnO-pigmented white paint degenerate, as shown in Fig. 1.

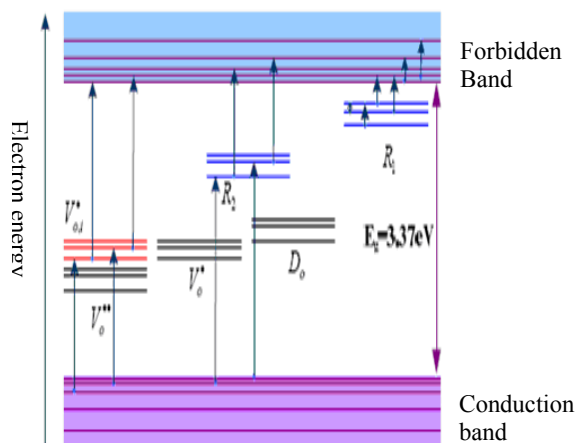


Fig. 1 Energy level and mechanism of degradation of optical characteristics of the ZnO-pigmented white paint by electron irradiation

III. MODEL OF SINGLE MOLECULAR COLOR CENTERS OF $\Delta\alpha_\lambda$ OF ZnO BY ELECTRON RADIATION

The density of color centers of ZnO increases by electron radiation. For getting the density of color centers of ZnO by electron radiation, ZnO are divided into single molecular layers, as shown in Fig. 2. We postulate that the lattice's density per layer is N_0 , the unit is cells/cm². The effective area of ZnO is s , the unit is cm². The integral flux of electron beam is Φ , the unit is ions/cm². The cross section of color centers that induced by electron radiation is σ , the unit is cm². The number of electrons that incidence at the surface is Φs and the number of color centers that induced in first layer is $\Phi\sigma$. Then the number of electrons that incidence at second layer is $\Phi(s-\sigma)$, and the number of color centers that induced in second layer is $\Phi(s-\sigma)\frac{\sigma}{s} = \Phi\sigma(1-\frac{\sigma}{s})$. By recursive computation, we know that the number of electrons that incidence at layer n is $\Phi(s-\sigma)(1-\sigma/s)^{n-2}$, and the number of color centers that induced in layer n is $\Phi\sigma(1-\frac{\sigma}{s})^{n-1}$. The density C of color centers that induced by electron radiation in whole ZnO can be described as:

$$C = \sum_{i=1}^n \frac{\sigma\Phi}{N_0 s} \left(1 - \frac{\sigma}{s}\right)^{i-1} \quad (1)$$

Totalizing equation 1 gives:

$$C = \frac{\Phi}{N_0} \left[1 - \left(1 - \frac{\sigma}{s}\right)^n \right] \quad (2)$$

Expanding equation 2 by an approximate solution gives:

$$C = \frac{\Phi\sigma}{N_0 s} n \quad (3)$$

where $n = \frac{d}{a_0}$, d is the range of electron in ZnO, a_0 is the

depth of the single molecular layer. The equation for photon intensity at a specific energy as a function of depth(x) in a material, $I(x)$, is given as follows by Beer law:

$$I(x) = I_0 e^{-ACx} \quad (4)$$

where I_0 is the photon intensity that incidence at the surface, x is the depth into the material, A is a constant independent with density. Differentiating Equation 4 gives:

$$\frac{\Delta I(x)}{I_0} = -AC\Delta x e^{-ACx} \quad (5)$$

where, Δx is an infinitesimal in mathematics, its significative physical quantity is a_0 . For a specific wavelength light, the absorptance of ZnO, $\alpha_{\lambda C}$, by electron radiation can be described as:

$$\alpha_{\lambda C} = \frac{\Delta I(d)}{I_0} = -A(C + C_0)a_0 e^{-A(C+C_0)d} \quad (6)$$

where C_0 is the density of the intrinsic color center, and the absorptance of ZnO before electron radiation, $\alpha_{\lambda 0}$, depends on it. $\alpha_{\lambda 0}$ is given as:

$$\alpha_{\lambda 0} = -AC_0 a_0 e^{-AC_0 d} \quad (7)$$

The change of absorptance between before and after electron radiation of ZnO, $\Delta\alpha$, is given as:

$$\Delta\alpha = \alpha_{\lambda C} - \alpha_{\lambda 0} \quad (8)$$

Substituting Equation 6 and 7 into Equation 8 gives:

$$\Delta\alpha = -ACa_0 e^{-A(C+C_0)d} - AC_0 a_0 e^{-AC_0 d} (e^{-ACd} - 1) \quad (9)$$

Substituting Equation 3 and 4 into Equation 9 gives:

$$\Delta\alpha = -K_1 \Phi e^{-K_2 \Phi} - K_3 (e^{-K_4 \Phi} - 1) \quad (10)$$

where K_1 , K_2 , K_3 , K_4 are constants that determined by A , N_0 , s , σ , d , a_0 .

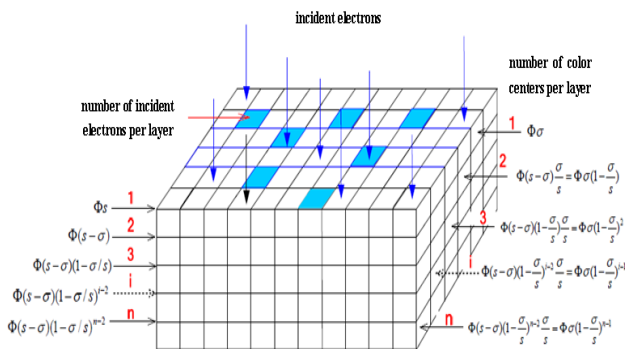


Fig. 2 Model of single molecular color centers by electron radiation

IV. RESULTS AND DISCUSSION

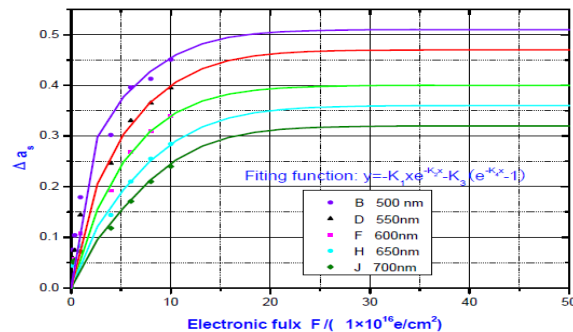
Simulation test of radiation stability of S781 white paint under electron irradiation with particle energy 100keV and particle fluence $1.0 \times 10^{17} \text{cm}^{-2}$ were done on the complex equipment for investigations of radiation stability of materials. S781 white paint is a typical ZnO-pigmented white paint. In the S781 white paint, the ratio of the ZnO and S781 silicone resin is 4:1^[4]. S781 silicone resin can also affect the absorbance. The refraction index determines the absorbance, and the ZnO has the high refraction index^[6]. Therefore, the S781 silicone resin's effects can be ignored.

Data on the S781 white paint tested are presented in Table I, where $\Delta\alpha_\lambda$ is the change of absorbance between before and after electron irradiation of ZnO at a specific wavelength.

TABLE I
DATA ON THE S781 WHITE PAINT TESTED UNDER ELECTRON IRRADIATION

Serial Number	electron fluence (e/cm^2)	$\Delta\alpha_\lambda$ 500nm	$\Delta\alpha_\lambda$ 550nm	$\Delta\alpha_\lambda$ 600nm	$\Delta\alpha_\lambda$ 650nm	$\Delta\alpha_\lambda$ 700nm
1	0	0	0	0	0	0
2	1.9×10^{15}	0.075	0.058	0.048	0.044	0.051
3	3.8×10^{15}	0.104	0.074	0.057	0.051	0.055
4	7.6×10^{15}	0.118	0.092	0.069	0.054	0.051
5	9.5×10^{15}	0.179	0.144	0.108	0.083	0.072
6	4.0×10^{16}	0.302	0.246	0.192	0.144	0.118
7	6.0×10^{16}	0.396	0.330	0.268	0.210	0.171
8	8.0×10^{16}	0.413	0.365	0.309	0.255	0.210
9	1.0×10^{17}	0.451	0.395	0.340	0.284	0.240

The uncertain parameters in the Equation 10 were calculated using the curve fitting by the experimental data in Table I. The result is shown in Fig. 3.

Fig. 3 The experimental data was compared with fitting curve of $\Delta\alpha_s$ of S781 white paint under electron irradiation

The coefficient matrix of fitting function in Fig. 3 is given as:

$$\begin{bmatrix} K_{500} & K_{550} & K_{600} & K_{650} & K_{700} \\ K_{2500} & K_{2550} & K_{2600} & K_{2650} & K_{2700} \\ K_{3500} & K_{3550} & K_{3600} & K_{3650} & K_{3700} \\ K_{4500} & K_{4550} & K_{4600} & K_{4650} & K_{4700} \end{bmatrix} \begin{bmatrix} 0.12 & 0.11 & 0.09 & 0.11 & 0.12 \\ 0.30 & 0.28 & 0.28 & 0.27 & 0.28 \\ 0.51 & 0.47 & 0.40 & 0.36 & 0.32 \\ 0.88 & 0.50 & 0.42 & 0.50 & 0.50 \end{bmatrix} \quad (11)$$

where $K_{i,\lambda}$ ($i=1,2,3,4$, $\lambda=500,550,600,650,700$) is the coefficient in Equation 10 of various wavelength lights of correspondence. The result indicates that the model of single molecular color centers explains the degradation of optical characteristics of S781 white paint under electron irradiation satisfactorily. Fig. 3 shows that:

(1) the change of absorbance ($\Delta\alpha_\lambda$) of S781 white paint tended to saturation with the increase of electron fluence, it's because the density of color centers of S781 white paint induced under electron irradiation achieves saturation with long-time electron irradiation. The optical characteristics are shown in Table II when the density achieves saturation.

(2) the change of absorbance ($\Delta\alpha_\lambda$) reduces as the wavelength increases, it's because photon energy decreases as the wavelength increases and photon energy is not big enough to induce that conduction band electrons jump to V_o^* or R_2 energy level, or the bound electrons in the V_o^* and R_2 color center level jump to conduction band. Significant color centers can not be generated.

TABLE II
THE PREDICTION OF OPTICAL CHARACTERISTICS OF S781 WHITE PAINT UNDER 100KEV ELECTRON IRRADIATION

wavelength of light incident $\lambda / (\text{nm})$	of electron fluence when the change of absorbance ($\Delta\alpha_\lambda$) achieves saturation $F / (1 \times 10^{16} \text{electrons}/\text{cm}^2)$	the change of absorbance ($\Delta\alpha_\lambda$) when it achieves saturation
500	21.04	0.507
550	23.48	0.467
600	28.60	0.399
650	30.32	0.360
700	32.90	0.320

V. CONCLUSION

In conclusion, based on energy band theory and color center theory, a model of single molecular color centers induced by electron radiation is built. An equation that explains the relationship between the changes of variation of the ZnO-pigmented white paint's spectrum absorptance and electron fluence is derived. The uncertain parameters in the equation were calculated using the curve fitting by the experimental data of ZnO-pigmented white paint under electron irradiation. The result indicates that the model of single molecular color centers explains the degradation of optical characteristics of ZnO-pigmented white paints under electron irradiation satisfactorily. The model parameters of K_1 , K_2 , K_3 , K_4 depend on the material parameters of A , N_0 , s , σ , d , a_0 and the numerical value can be determined by curve fitting.

This model can be used to accurately predict the optical performance degradation under space electron radiation. On this basis, we can build the solar absorbance variation model, which is more useful for the engineering.

REFERENCES

- [1] Broadway N J. Radiation effects design handbook Section 2:thermal control coating [R]. N-71-32280.
- [2] Sony Youhao. Experiment of combined space environmental effects of electron, proton, ultraviolet and atom oxygen [J] . Environment simulation technology. 1994(2):14,22(in Chinese)
- [3] Michael H.Huang, Yiyi Wu, Henning Feik, Ngan Tran.Catalytic growth of zinc oxide nanowires by vapor transport. Advanced Materials. 2001,13(2): 113~116
- [4] Kroger F A The chemistry film perfect crystals[M]. Amsterdam: North-Holland Publishing Company, 1964
- [5] Wang Xu-dong, HE Shi-yu, Yang De-zhuang. Dependence of ZnO/K₂SiO₃ thermal control coating optical characteristics upon electron exposure. High Power Laser and Particle Beams, 2001, 13 (4) : 431-435 (in Chinese)
- [6] Zhao Feiming, Zhang Lianzheng, Zeng Yibing et al. The Recent Development of Silicone Thermal Control Coatings with a Low Ratio of Spectral Absorptances as to Emittances ϵ . Aerospace Materials & Technology.1998,(3):11~14 (in Chinese)